

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : **11-192777**

(43)Date of publication of application : **21.07.1999**

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(51)Int.Cl. **B41M 5/00**  
**B41M 5/38**  
**G03G 7/00**

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## **(54) RECORDING SHEET**

### **(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide a recording sheet having a colorant receptive layer including an excellent water resistance to be easily formed with scarce crack at the time of coating and drying by obtaining an image sheet by an ink jet recording, thermal transfer recording or an electrophotographic recording.

**SOLUTION:** In the recording sheet comprising a colorant receptive layer on a support, the receptive layer is a water soluble resin cured film containing inorganic fine particles and a mordant. The sheet preferably has the colorant receptive layer obtained by coating the support with the fine particles and water soluble resin, giving a solution containing a crosslinker for crosslinking the resin and the mordant simultaneously with the coating or before the coated layer exhibits a falling drying speed and curing it.

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## **LEGAL STATUS**

[Date of request for examination] **12.03.2004**

[Date of sending the examiner's decision of  
rejection]

[Kind of final disposal of application other  
than the examiner's decision of rejection or  
application converted registration]

[Date of final disposal for application]

[Patent number] **3907811**

[Date of registration] **26.01.2007**

[Number of appeal against examiner's  
decision of rejection]

[Date of requesting appeal against

examiner's decision of rejection]

[Date of extinction of right]

## CLAIMS

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[Claim(s)]

[Claim 1] The sheet for record characterized by being the hardening film of the water soluble resin with which this color-material acceptance layer contains a non-subtlety particle and a mordant in the sheet for record with which the color-material acceptance layer is prepared on the base material.

[Claim 2] The sheet for record according to claim 1 which is the layer obtained by this color-material acceptance layer's applying the coating liquid containing a non-subtlety particle and water soluble resin on a base material, giving the solution which contains the cross linking agent which can construct a bridge in this water soluble resin, and a mordant this spreading, coincidence, or before the applied this layer comes to show the falling rate of drying, and making it harden.

[Claim 3] The sheet for record according to claim 1 which is the layer obtained by carrying out coincidence spreading and making it harden on a base material where the barrier liquid (however, either [ at least ] the solution containing a cross linking agent or barrier liquid is made to contain a mordant) with which this color material acceptance layer consists the coating liquid containing a non-subtlety particle and water soluble resin and the solution containing a cross linking agent of this cross linking agent and an ingredient which does not react is inserted.

[Claim 4] The sheet for record given in claim 1 whose cross linking agent is a boron compound thru/or the term of either of 3.

[Claim 5] The sheet for record given in claim 1 whose primary [ an average of ] particle diameter a non-subtlety particle is a silica particle 20nm or less thru/or the term of either of 4.

[Claim 6] The sheet for record given in claim 1 whose water soluble resin is polyvinyl alcohol thru/or the term of either of 5.

[Claim 7] The sheet for record given in claim 1 which has the weight ratio of a non-subtlety particle and water soluble resin in the range of 1.5:1-10:1 thru/or the term of either of 6.

[Claim 8] The sheet for record given in claim 1 in which a color-material acceptance layer has 40 - 80% of voidage thru/or the term of either of 6.

[Claim 9] The sheet for record given in claim 1 whose mordant is a basic polymer thru/or the term of either of 8.

[Claim 10] The sheet for record given in claim 1 which is an object for ink jet record thru/or one term of 9.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the sheet for record which records an image (it is a concept also containing an alphabetic character image) etc. using color

material. In order to form an image sheet by ink jet record, thermal transfer recording, electrophotography record, etc. especially, it is related with the sheet for record used advantageously.

[0002]

[Description of the Prior Art] In recent years, the recording method and equipment which various information processing system was developed and fitted each information system are also developed and adopted with rapid development of an information industry. It is known that lightweight-sizing and the miniaturization of equipment which the thermal-ink-transfer-printing recording method using an ink jet or the ink recording method using a plotter and melting mold color material, or sublimation mold color material uses are easy, and the noise does not have them, either, and they are excellent also in operability and maintainability in such a recording method. Moreover, by such recording method, formation of a color picture is also easy. In addition, also by the record system of the conventional electrophotography method, colorization progresses, and the printer and copying machine in which full color \*\* is possible have been developed and commercialized with high resolution.

[0003] Although various kinds of methods are developed as an ink jet method, there are three sorts, the approach using the coloring matter solution (water color ink) which roughly divides and contains water-soluble coloring matter, the approach using the coloring matter solution (oily ink) containing oil solubility coloring matter, and the method of carrying out thermofusion of the low-melt point solid wax (wax ink) containing coloring matter, and using it. The mainstream is a type which uses water color ink. Any approach is the approach of forming an image by the approach of solidifying ink by making the front face of the sheet for ink record breathe out the particle drop of ink, and performing desiccation or cooling after that.

[0004] A thermal-ink-transfer-printing method is roughly divided, and has two sorts of methods. The first method by carrying out heat impression from a base material side at the shape of a pattern on the ink sheet with which the ink layer of thermofusion nature was formed on the base material. It is the approach (heat-of-fusion imprint) of carrying out melting of the ink layer to the shape of a pattern, making the sheet for record imprinting the melting ink, and obtaining an image. The second method is the approach (heat-of-sublimation imprint) of performing heat impression from a base material side into the thermal recording ingredient in which the ink layer which consists of the resin and the sublimability color of high softening temperature was formed on the base material, like the former, making a sublimation color sublimating to it in the shape of a pattern, making an ink image imprinting on the sheet for record, and obtaining an image. After giving an optical image pattern to the electrified photoconductive layer by the electrophotography method, forming an electrostatic latent image and developing negatives with a toner subsequently, the approach of imprinting a toner image on the sheet for record, and carrying out melting fixing of the toner with heat is in use.

[0005] On the other hand, it may be necessary to form an image on a transparency sheet. In this case, a transparency image is imprinted on the sheet for transparency record using either of the above-mentioned approaches using the bright film which prepared the transparent color-material acceptance (absorption) layer in the front face as a sheet for record. By forming a transparency image on such a sheet for transparency record, the OHP film used instead of a slide, the film for a back light display used instead of a

printing poster or a display board, the film for mother prints, etc. are created.

[0006] The sheet for record (bright film) in which the image (a transparency image or light transmission nature image) was formed by the above-mentioned recording method When it is required for the color material which needs to show the hue excellent in the image obtained, saturation, and lightness, and forms the image further to have pasted the front face of the sheet for record firmly and the still more minute image in the case of ink jet record is obtained Liquefied ink is absorbed early and it is required that neither an ink blot nor ink \*\*\*\*\* should be generated etc.

[0007] In order to solve these troubles, various proposals are made from the former. For example, the sheet for record which becomes JP,57-14091,A and JP,61-19389,A from the clear layer of a transparency base material, and the colloidal silica and water soluble resin which were prepared on it is proposed. However, as for this clear layer, since the particle of colloidal silica is too large and there are too many amounts of water soluble resin, voidage big enough is not obtained, but for this reason, the above-mentioned sheet for record has the problem that ink rate of absorption large enough is hard to be shown.

[0008] Moreover, the sheet for record possessing the color-material acceptance layer which has the pore formed from the quasi-boehmite particle is indicated by JP,2-276670,A and JP,3-281383,A. According to examination of this invention person, although this sheet for record showed high ink absorptivity, since the refractive index was high, it became clear that transparency high enough was not acquired.

[0009] The sheet for record which has the clear layer which becomes JP,61-53598,A from a base material, and the particle and water soluble resin of a synthetic silica and refractive indexes 1.44-1.55 which were prepared on it further again is indicated. A synthetic silica has a diameter of a primary particle usually exceeding 10nm, and an aggregated particle serves as particle size of several 100nm further. The sheet for record containing such a particle does not show light transmittance high enough that such aggregated particles tend to be scattered [ therefore ] about in light. Furthermore, since a clear layer is a big aggregated particle and it has comparatively many holes, generating of an ink blot or ink \*\*\*\*\* cannot fully be prevented.

[0010] The sheet for record with which the color-material acceptance layer which has the three-dimensional structure of the high voidage formed in JP,7-276789,A from a non-subtlety particle and water soluble resin as a sheet for record which solves the above-mentioned problem was prepared on the transparency base material is proposed. Control of the above-mentioned ink absorptivity and a color mixture blot is presupposed by this configuration that it is enough and an image with high resolution can be obtained.

[0011]

[Problem(s) to be Solved by the Invention] This invention sets it as the main purposes to offer the non-subtlety particle and water soluble resin in which high transparency and the outstanding color-material stability are shown, or the sheet for record equipped with the becoming color-material acceptance layer.

[0012] In addition, generally, the non-subtlety particle used in the color-material acceptance layer of the high voidage formed from a non-subtlety particle and water soluble resin has a small particle, and it is [ the content of the particle in a color-material acceptance layer ] large. And when the coating liquid containing the ingredient for forming such a color-material acceptance layer was applied, while drying the spreading layer, it became clear by examination of this invention person that a cracking crack may

occur. And especially this cracking crack became clear [ that it is also easy to generate when it dries at comparatively high temperature ], in order to shorten the drying time. Although the approach of making viscosity of the binder of coating liquid comparatively high is proposed by JP,9-109545,A as an approach of preventing this cracking crack, since it is easy to generate spreading nonuniformity etc. and leads to the fall of the workability of spreading formation of a color-material acceptance layer by this approach, it is not desirable. Moreover, this approach cannot be said to be enough in the cracking crack prevention effectiveness.

[0013] In order to prevent the cracking crack of the above-mentioned color-material acceptance layer, this invention person repeated examination, and the cracking crack of a spreading layer became clear [ generating at the stage shifting to decreasing drying ] in the middle of the desiccation (i.e., constant rate drying), after applying the coating liquid for color-material acceptance stratification on a base material. Based on this knowledge, this invention person repeated examination further and completed invention of the sheet for record which prepared it as early as possible as raised the film reinforcement of a spreading layer in the condition of the constant rate drying before a decreasing drying condition starts. This invention is indicated by the Japanese-Patent-Application-No. No. 296285 [ nine to ] specification. In addition, although the example which applied the silane coupling agent on porous membrane, and gave the water resisting property was shown by this application, as a result of this invention person's repeating examination, a header and this invention were reached [ that waterproof improvement is possible and ] also by applying a mordant to a cross linking agent and coincidence.

[0014] Therefore, it also sets it as the purpose that this invention can obtain an image sheet by ink jet record, thermal transfer recording, or electrophotography record, and offers the sheet for the record which has the color-material acceptance layer excellent in the water resisting property which a cracking crack cannot generate easily at the time of spreading desiccation, and can be formed simply.

[0015] Especially this invention can form a minute image, without preventing the absorption nonuniformity of ink and generating an ink blot and ink \*\*\*\*\* by absorbing liquefied ink quickly, and it aims at offering the sheet for record equipped with the color-material acceptance layer excellent in the water resisting property which can be formed simply suitable for especially ink jet record, without a cracking crack occurring at the time of spreading desiccation.

[0016]

[Means for Solving the Problem] This invention is in the sheet for record characterized by being the hardening film of the water soluble resin with which this color-material acceptance layer contains a non-subtlety particle and a mordant in the sheet for record with which the color-material acceptance layer is prepared on the base material. A color-material acceptance layer applies the coating liquid containing a non-subtlety particle and water soluble resin on a base material again, and this invention is also in the spreading and coincidence, or the above-mentioned sheet for record which is the layer obtained by giving and stiffening the solution containing the cross linking agent which can construct a bridge in water soluble resin, and a mordant before the applied layer comes to show the falling rate of drying. This invention is also in the above-mentioned sheet for record which is the layer obtained by carrying out coincidence spreading and making it harden on a base material where the barrier liquid (however, either [ at least ] the solution

containing a cross linking agent or barrier liquid is made to contain a mordant) with which a color material acceptance layer consists the coating liquid containing a non-subtlety particle and water soluble resin and the solution containing a cross linking agent of a cross linking agent and an ingredient which does not react again is inserted.

[0017] The desirable mode of the sheet for record of this invention is as follows.

- (1) A cross linking agent is a boron compound (especially borax).
- (2) A non-subtlety particle is [ primary / an average of / particle diameter ] a silica particle 20nm or less (preferably 10nm or less, especially the range of 3-10nm).
- (3) Water soluble resin is polyvinyl alcohol or gelatin.
- (4) The weight ratio of a non-subtlety particle and water soluble resin is in the range of 1.5:1-10:1 (subtlety [ non- ] particle: water soluble resin).
- (5) A color-material acceptance layer has 40 - 80% of voidage (especially 50 - 80% of voidage).

[0018] (6) The sheet for record is an object for ink jet record.

(7) The coverage on the color-material acceptance layer of a cross linking agent content solution is 0.01 - 10 g/m<sup>2</sup> in the amount of cross linking agent conversions. It is in the range (especially the range of 0.05 - 5 g/m<sup>2</sup>).

- (8) A color-material acceptance layer has a three-dimensional network.
- (9) A color-material acceptance layer has 30% or less of Hayes.
- (10) The above-mentioned sheet for record for ink jet record whose thickness of a color-material acceptance layer is 10-50 micrometers.
- (11) The object for electrophotography or the sheet for the above-mentioned record for thermal recording whose thickness of a color-material acceptance layer is 0.1-10 micrometers.
- (12) The mordant contained in a color-material acceptance layer is a basic polymer.

[0019]

[Embodiment of the Invention] The sheet for record of this invention has the basic configuration which consists of a base material and a color-material acceptance layer formed on the base material, for example, can manufacture it as follows.

[0020] Opaque ingredients, such as paper, may be used, using transparent materials, such as plastics, as an ingredient which can be used as a base material. When employing the transparency of a color-material acceptance layer efficiently in this invention, as for a base material, it is desirable that they are a transparence base material or the opaque base material of high gloss. As an ingredient which can be used as a transparence base material, it is transparent and the ingredient which has the property to bear the radiant heat when being used on OHP or a back light display is desirable. As such an ingredient, cellulose ester, such as polyester; nitrocelluloses, such as polyethylene terephthalate, cellulose acetate, and cellulose acetate butylate, and polysulfone, polyphenylene oxide, polyimide, a polycarbonate, a polyamide, etc. can be mentioned. Polyester is desirable in these and especially polyethylene phthalate is desirable. About the thickness of a transparence base material, although there is especially no limit, its 50-200-micrometer thing is easy to deal with it and is desirable.

[0021] That in which the near front face in which a color-material acceptance layer is prepared has 40% or more of glossiness as an opaque base material of high gloss is desirable. The above-mentioned glossiness is JIS. It is the value calculated by measuring according to the approach of a publication to P-8142 (75-degree specular gloss test

method of paper and the paper board). As an example of the opaque base material of high gloss, art paper, coat paper, cast coated paper, Paper of high gloss, such as a baryta paper used for the base material for film photos etc.; Polyester, such as polyethylene terephthalate (PET) Cellulose ester, such as a nitrocellulose, cellulose acetate, and cellulose acetate butylate Or polysulfone, polyphenylene oxide, polyimide, a polycarbonate, The film of the high gloss which plastic film, such as a polyamide, was made to contain white pigments etc., and was made opaque (surface calender processing etc. is performed), Or the film with which the enveloping layer of the polyolefine which contains white pigments or is not contained was prepared in the front face of content plastics, such as the various above-mentioned papers, the above-mentioned transparency plastic film, or white pigments, can be mentioned. Furthermore, white-pigments content foaming polyester film (calcium content foaming PET which was made to contain an example and a polyolefine particle and formed the opening by extension) can also be mentioned. Moreover, the special kind paper in which the polyolefine coat paper (paper base material with which the white-pigments content polyolefine layer was prepared in the front face) currently generally used as a base material for film photos, or a metal vacuum evaporationo layer was prepared can be used suitably. The paper base material with which the white-pigments content polyolefine layer was prepared especially, the polyester (preferably PET) film with which the white-pigments content polyolefine layer was prepared, white-pigments content polyester film, or white-pigments content foaming polyester film is desirable. Even if it attaches the thickness of an opaque base material, although there is especially no limit, a 50-200-micrometer thing is easy to deal with it and is desirable [ a limit ].

[0022] As a base material, what performed corona discharge treatment, flame treatment, and UV irradiation processing may be used.

[0023] In case the coating liquid containing a non-subtlety particle and water soluble resin is applied on a base material, this spreading, coincidence, or before the applied this layer comes to show the falling rate of drying, as for the color-material acceptance layer of the sheet for record of this invention, it is desirable that it is the layer which the water soluble resin obtained by giving and stiffening the solution containing a cross linking agent and a mordant on a spreading layer hardened by the cross linking agent.

[0024] Moreover, the color-material acceptance layer of the sheet for record of this invention can also be obtained by carrying out coincidence spreading and making it harden on a base material, where the barrier liquid (however, either [ at least ] the solution containing a cross linking agent or barrier liquid is made to contain a mordant) which consists the coating liquid containing a non-subtlety particle and water soluble resin and the solution containing a cross linking agent of a cross linking agent and an ingredient which does not react is inserted.

[0025] The polyvinyl alcohol which is resin which has hydroxyl as a hydrophilic structural unit as an example of water soluble resin (PVA), Cellulose system resin [methyl cellulose (MC), ethyl cellulose (EC), ], such as hydroxyethyl cellulose (HEC) and a carboxymethyl cellulose (CMC), Chitins and starch; The polyethylene oxide which is resin which has ether linkage (PEO), The polyacrylamide (PAAM) and the polyvinyl pyrrolidone (PVP) which are resin which has polypropylene oxide (PPO), polyethylene-glycol (PEG), and polyvinyl ether (PVE);, an amide group, and amide association can be mentioned. Moreover, the polyacrylate which has a carboxyl group as a dissociative

radical, maleic resin, alginate, and gelatin can be mentioned.

[0026] As a non-subtlety particle, a silica particle, colloidal silica, a calcium silicate, a zeolite, a kaolinite, halloysite, a muscovite, talc, a calcium carbonate, a calcium sulfate, boehmite, quasi-boehmite, etc. can be mentioned, for example. What has a refractive index in the range of 1.40-1.60 from the point of not reducing transparency is desirable. A silica particle is desirable in these. Moreover, the first [ an average of ] particle diameter of a non-subtlety particle has a common thing 20nm or less (preferably 10nm or less, especially 3-10nm), and, as for a refractive index, it is desirable that they are the 1.45 neighborhoods.

[0027] By the hydrogen bond by the surface silanol group, for an adhesion and cone reason, particles can form the structure where especially voidage is large, when especially the first [ an average of ] particle diameter is 10nm or less as mentioned above, and the ink absorption property of a silica particle improves. A silica particle is divided roughly into a wet method particle and a dry-process particle according to a manufacturing method. The method of the acidolysis of a silicate generating active silica, carrying out the polymerization of this moderately in a wet method, carrying out flocking settling, and obtaining a water silica is in use. One dry process has a method in use of obtaining an anhydrous silica by the approach (arc process) of carrying out heating hydride generation of the approach (flame hydrolysis), silica sand, and corks by elevated-temperature gaseous-phase hydrolysis of halogenation silicon with an arc in an electric furnace, and oxidizing this with air. In the case of a silicic anhydride (anhydrous silica), especially voidage is easy to form the high three-dimensional structure and is desirable [ a silica ], although the water silica and the anhydrous silica which are obtained by these approaches have a difference in the consistency of a surface silanol group, the existence of a hole, etc. and show a property different, respectively. This reason is 2 5-8 pieces/nm, when the consistency of a surface silanol group is a water silica, although it is not clear. Mostly, when it is easy to condense a particle densely (aggregate) and it is one anhydrous silica, it is 2 2-3 pieces/nm. Since it is few, it is presumed that it is because it becomes \*\*\*\* flocculation (FUROKYU rate) and voidage becomes high structure.

[0028] When the class of resin combined with a silica particle is important and it uses an anhydrous silica from a viewpoint of transparency, PVA, especially PVA of whenever [ low saponification ] (whenever [ saponification ] is 70 - 90% preferably) are suitable from the point of light transmission nature as water soluble resin. Although PVA has a hydroxyl group in a structural unit, this hydroxyl group and the silanol group of a silica particle front face make easy to form the three-dimensional network which forms hydrogen bond and makes the aggregated particle of a silica particle a chain unit, and it is thought that the color-material acceptance layer of the structure where voidage is high is formed by this. Thus, not only the minute record which absorbs ink quickly by capillarity and has neither an ink blot nor ink \*\*\*\*\* is possible, but the obtained porous layer can paste up firmly the color material in thermal recording, and the toner in electrophotography record in ink jet record. Color material and a toner permeate in the pore of a porous layer, the geometrical anchor effect which originates in a three-dimensional network as that result generates this reason, and it is understood that it is because this fixes color material etc. firmly. Moreover, since the rate of a non-subtlety particle increases, thermal resistance is high and the embossing-proof nature in electrophotography record also has the description of being high.

[0029] The ratio (PB ratio: weight of the non-subtlety particle to the weight 1 of water soluble resin) of a non-subtlety particle (preferably silica particle) and water soluble resin has big effect also on the membrane structure of a color-material acceptance layer. If PB ratio becomes large, voidage, pore volume, and surface area (per unit weight) will become large. If PB ratio exceeds 10, there is no effectiveness over film reinforcement and the cracking crack at the time of desiccation, on the other hand, less than by 1.5, an opening should tend to be closed by resin, voidage will decrease, and ink absorptivity ability will fall. For this reason, the range of 1.5-10 is suitable for PB ratio. Like especially an OHP film, to touch the image of the sheet for record directly by hand in many cases, a color-material acceptance layer needs to show sufficient film reinforcement. In this case, as for PB ratio, it is desirable that it is especially five or less, and in order to acquire high-speed ink absorptivity with an ink jet printer, as for PB ratio, it is desirable that it is two or more, and it is suitable that it is especially in the range of 2-5.

[0030] For example, when the first [ an average of ] particle diameter carries out spreading desiccation of the coating liquid which distributed completely [ PB ratio / 2-5 ] in a water solution an anhydrous silica and water soluble resin 10nm or less, the three-dimensional network which makes the aggregated particle of a silica particle a chain unit is formed, 30nm or less and voidage can form 0.5 or more mL/g of pore specific volume, and specific surface area can form [ average pore ] easily the porous membrane of the translucency 100m<sup>2</sup> / more than g 50% or more.

[0031] The color-material acceptance layer of the sheet for record of this invention is a layer which the cross linking agent and the mordant were given to the layer (porous layer) which uses a non-subtlety particle and water soluble resin as a principal component, and water soluble resin hardened by the cross linking agent. As for grant of a cross linking agent, it is desirable to be carried out before the coating liquid layer for porous layer formation comes to show the falling rate of drying at the same time the above-mentioned coating liquid for porous layer formation is applied. The cracking crack generated by this actuation while the spreading layer of the coating liquid for porous layer formation dries can be prevented effectively. That is, before a spreading layer comes to show the falling rate of drying at the same time the above-mentioned coating liquid for porous layer formation was applied or, the film reinforcement of a spreading layer is immediately raised sharply by a cross linking agent content solution's permeating in a spreading layer, reacting promptly with the water soluble resin in a spreading layer, and making water soluble resin macromolecule-ize (hardening). Consequently, the cracking crack generated at the time of desiccation of the spreading layer of the above-mentioned coating liquid for porous layer formation can be prevented effectively.

[0032] As an example of the cross linking agent used for formation of the color-material acceptance layer of the sheet for record of this invention borax, boric acid, and borate (an example, an orthoboric salt, InBO<sub>3</sub>, and ScBO<sub>3</sub> --) YBO<sub>3</sub>, LaBO<sub>3</sub>, Mg<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, and Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, diborate (an example, Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub>, Co<sub>2</sub>B<sub>2</sub>O<sub>5</sub>) and a metaboric acid salt (an example --) LiBO<sub>2</sub>, calcium (BO<sub>2</sub>)<sub>2</sub>, and NaBO<sub>2</sub> and KBO<sub>2</sub>, tetraborate (example and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and 10H<sub>2</sub>O) and 5 borate (an example --) KB<sub>5</sub>O<sub>8.4</sub>H<sub>2</sub>O and calcium<sub>2</sub>B<sub>6</sub>O<sub>11</sub> and 7H<sub>2</sub>O, CsB<sub>5</sub>O<sub>5</sub>, glyoxal, melamine formaldehyde (an example, a methylol melamine, alkylation methylol melamine), a methylolurea, resol resin, the poly isocyanate, etc. can be mentioned. Borax, boric acid, or borate is desirable in these. Since

using it combining polyvinyl alcohol as water soluble resin causes crosslinking reaction promptly, borax, boric acid, and borate have it. [ desirable ]

[0033] When using gelatin as water soluble resin, the following compound known as a hardening agent of gelatin can be used as a cross linking agent. Aldehyde system compounds, such as formaldehyde, glyoxal, and a glutaraldehyde; Diacetyl, Ketone system compounds, such as cyclopentane dione; bis(2-chloro ethylurea)-2-hydroxy - 4, 6-dichloro-1,3,5-triazine, Activity halogenated compounds, such as 2 and 4-dichloro-6-S-triazine sodium salt; A divinyl sulfonic acid, A 1, 3-vinyl sulfonyl-2-propanol, N, and N'-ethylene screw (vinyl sulfonyl acetamido), Activity vinyl compounds, such as 1, 3, and 5-thoria chestnut roil-hexahydro-S-triazine; A dimethylolurea, N-methylol compound [, such as methylol dimethylhydantoin, ]; -- isocyanate system compound [, such as 1,6-hexamethylene diisocyanate, ]; -- U.S. Pat. No. 3017280 -- Aziridine system compound; indicated by 2983611 Ethyleneimino compound, such as an epoxy compound;1, such as carboximide compound; glycerol triglycidyl ether indicated by U.S. Pat. No. 3100704, 6-hexamethylene-N, and N'-screw ethylene urea; Mucochloric acid, Halogenation carboxy aldehyde system compounds, such as a mucophenoxy KURORU acid; dioxane system compound; chromium alum, such as 2 and 3-dihydroxy dioxane, potash alum, a sulfuric-acid zirconium, chromium acetate, etc. In addition, two or more sorts can be combined and these hardening agents (cross linking agent) can also be used, even if independent.

[0034] The solution of a cross linking agent dissolves a cross linking agent in water and/or an organic solvent, and is prepared. The cross linking agent concentration in a cross linking agent solution has 0.05 - 10 desirable % of the weight, and its 0.1 - 7 % of the weight is especially desirable. Generally as a solvent of a cross linking agent, water is used. As an organic solvent, if a cross linking agent dissolves, it can be used for arbitration, for example, halocarbon system solvents, such as the ether [, such as ester; toluene, /, such as an aromatic series solvent; tetrahydrofuran, ], such as ketone; methyl acetate, such as alcoholic; acetones, such as a methanol, ethanol, and isopropyl alcohol, and a methyl ethyl ketone, and ethyl acetate, and dichloromethane, etc. can be mentioned.

[0035] In addition, in this invention, the water resisting property is raised by applying a mordant with a cross linking agent. If a mordant is added to the coating liquid for porous layer formation, condensation may be produced for the cationicity of the anion charge of the front face of non-subtlety particles, such as a silica, and a mordant, but each is prepared as an independent solution, if the approach of applying is used, there will be no worries about condensation of non-subtlety particles, such as a silica, and the selection range of a mordant will spread.

[0036] As a mordant, an amide group, an imide radical, the 1st class amino group, the 2nd class amino group, It is a compound containing at least one sort of cation radicals chosen from the 3rd class amino group, the 1st class ammonium salt radical, the 2nd class ammonium salt radical, the 3rd class ammonium salt radical, and a quarternary-ammonium-salt radical. As the example Polyvinylbenzyl trimethylammoniumchloride, polydiallyldimethylammoniumchloride, Polymethacryloyloxyethyl-beta-hydroxyethyltrimethylammoniumchloride, A poly dimethylaminoethyl methacrylate hydrochloride, polyethylene RENIMIN, The poly allylamine, the poly allylamine hydrochloride, polyamide-polyamine resin, cation-ized starch, a dicyandiamide formalin condensate, a dimethyl-2-hydroxypropyl ammonium salt polymerization object, etc. can be mentioned. As for molecular weight, 1000 to about 20000 are [ these compounds ]

desirable. There is an inclination for molecular weight to become insufficient [ less than 1000 / a water resisting property ], or more by 200000, viscosity becomes high and handling fitness serves as a defect.

[0037] When the coating liquid (coating liquid for porous layer formation) which uses a non-subtlety particle and water soluble resin as a principal component is applied on a base material on the occasion of manufacture of the sheet for record of this invention, it is desirable to use the approach of giving a cross linking agent so that this spreading layer may not cause a cracking crack, raising the film reinforcement of a spreading layer promptly, and giving a mordant to coincidence and raising a water resisting property. Or [ it applies the solution which contains a cross linking agent and a mordant in spreading and coincidence of the coating liquid which uses a non-subtlety particle and water soluble resin as a principal component in fact (it is desirable to make the barrier liquid which consists of a cross linking agent and an ingredient which does not react intervene between the solutions containing the coating liquid and the cross linking agent which use a non-subtlety particle and water soluble resin as a principal component in this case, and a mordant.) ] In addition, or it may make barrier liquid contain a mordant, after applying the coating liquid which uses a non-subtlety particle and water soluble resin as a principal component in this case, it is desirable to use the approach of giving the solution which contains a cross linking agent and a mordant promptly.

[0038] Next, after applying the coating liquid (coating liquid for porous layer formation) which uses a non-subtlety particle and water soluble resin as a principal component, before the spreading layer comes to show the falling rate of drying, how to give the solution which contains a cross linking agent and a mordant promptly is explained.

[0039] the coating liquid for porous layer formation -- an average of 1 [ for example, ] -- the silica particle not more than order particle diameter 10nm -- underwater -- adding (an example --) A high-speed rotation wet colloid mill (an example, KUREA mix (M Technique Co., Ltd. make)) is used ten to 20% of the weight. For example, after carrying out distribution for 20 minutes (preferably for 10 - 30 minutes) on condition that high-speed rotation of 10000rpm (preferably 5000 - 20000rpm), A polyvinyl alcohol water solution (for example, it is set to PVA of about 1/3 weight of a silica like) can be added, and it can obtain by distributing on the still more nearly same conditions as the above. Thus, the obtained coating liquid is a homogeneity sol and can obtain the porous layer which has a three-dimensional network by forming this on a base material by the following method of application.

[0040] Spreading of the coating liquid for porous layer formation can be carried out by applying the coating liquid which added the antistatic agent etc. further by request and was obtained on a base material (film). Spreading can be performed by the well-known methods of application, such as an extrusion die coater, the Ayr doctor coater, bread coater, rod coater, knife coater, squeeze coater, a reverse roll coater, and bar coater.

[0041] After spreading of the coating liquid for porous layer formation, before the spreading layer comes to show the falling rate of drying, the solution containing the cross linking agent and mordant of this invention is applied on a spreading layer by the same approach as the above-mentioned coating liquid for porous layer formation, it can dry and the color-material acceptance layer by which this invention was hardened can be obtained. In addition, the solution containing a cross linking agent and a mordant may be given by the approach of a spray etc.

[0042] Before the above-mentioned spreading layer comes to show the falling rate of drying, the constant rate of drying which is for several minutes after immediately after spreading, and is the phenomenon in which the content of the solvent in a spreading layer decreases in proportion to time amount in the meantime is usually shown. The time amount which shows such the constant rate of drying is indicated by the chemical engineering handbook (707-712 pages, the Maruzen Co., Ltd. issue, October 25, Showa 55).

[0043] After spreading of the coating liquid for porous layer formation, the color-material acceptance layer of the sheet for record of this invention is preferably manufactured by giving the solution containing a cross linking agent and a mordant by the approach of spreading or a spray, while this spreading layer shows the constant rate of drying.

Generally desiccation after spreading of the coating liquid for porous layer formation is performed at 50-180 degrees C for 0.5 - 10 minutes (especially for 0.5 - 5 minutes).

Although this drying time naturally changes with coverage, the above-mentioned range is suitable for it.

[0044] A cross linking agent and a mordant can also be introduced into the spreading layer of the coating liquid for porosity formation that the base material which has this spreading layer is immersed in the solution which contains a cross linking agent and a mordant within the period the spreading layer indicates the constant rate of drying to be at the spreading layer of the coating liquid for porous layer formation, or by carrying out the spray coating cloth of the solution which contains a cross linking agent and a mordant in a spreading layer. Although the well-known methods of application other than the above-mentioned approach, such as a curtain flow coater, an extrusion die coater, the Ayr doctor coating machine, bread coater, rod coater, knife coater, squeeze coater, a reverse roll coater, and bar coater, can be used on the occasion of spreading of the coating liquid containing a cross linking agent and a mordant, it is desirable to use how coater does not contact a spreading layer directly using extrusion die coater, a curtain flow coater, bar coater, etc.

[0045] The coverage on the color-material acceptance layer of the coating liquid containing a cross linking agent and a mordant is 0.01 - 10 g/m<sup>2</sup> by cross linking agent conversion. The range is common and it is 0.05 - 5 g/m<sup>2</sup>. The range is desirable. After spreading of the coating liquid containing a cross linking agent and a mordant, generally a spreading layer is heated for 0.5 - 30 minutes at 40-180 degrees C, and desiccation and hardening are performed. It is desirable to heat in 1 - 20 minutes at 40-150 degrees C. For example, when using borax and boric acid as a cross linking agent, it is desirable to perform heating at 60-100 degrees C for 5 - 20 minutes.

[0046] Next, how to apply the solution which contains a cross linking agent and a mordant in spreading and coincidence of the coating liquid (coating liquid for porous layer formation) which uses as a principal component the non-subtlety particle and water soluble resin which are the another formation approach of the color-material acceptance layer of the sheet for record of this invention is explained. This approach can be acquired when it carries out coincidence spreading on a base material as the coating liquid for porous layer formation contacts a base material, and it stiffens the solution containing the coating liquid for porous layer formation and a cross linking agent, and a mordant. Coincidence spreading of the solution containing the coating liquid for porous layer formation and a cross linking agent, and a mordant can be performed by the method of

application which uses an extrusion die coater and a curtain flow coater, for example. Generally desiccation after coincidence spreading (multistory spreading) is performed by heating a spreading layer for 0.5 - 10 minutes at 40-150 degrees C, and a spreading layer is hardened. It is desirable to heat a hardening layer for 0.5 - 5 minutes at further 40-100 degrees C. For example, when using borax and boric acid as a cross linking agent, it is desirable to heat for 5 - 20 minutes at 60-100 degrees C.

[0047] When an extrusion die coater performs the above-mentioned multistory spreading, multistory is formed before two sorts of coating liquid moves to the delivery neighborhood of an extrusion die coater, i.e., a base material top. And since crosslinking reaction already tends to occur by the interface of a bilayer in case the spreading layer (multistory) of a bilayer moves to a base material, it becomes easy to generate thickening by mixing of regurgitation coating liquid near the delivery of an extrusion die coater, and trouble may be caused to spreading actuation. Therefore, in case the above-mentioned coincidence spreading is performed, it is desirable to apply it three layers of coincidence with spreading of the solution containing the coating liquid for porous layer formation and a cross linking agent, and a mordant, as the barrier layer solution (interlayer liquid) which serves as a cross linking agent from the ingredient which does not react further is made to intervene among both coating liquid. Barrier layer solution should just choose what does not react with a cross linking agent but can form liquid membrane. For example, a minute amount \*\*\*\* water solution and water can be mentioned for a cross linking agent and the water soluble resin (it is used as a thickener) which does not react. As an example of the polymer used in consideration of spreading nature, the hydroxypropyl methylcellulose, methyl cellulose, hydroxyethyl methyl cellulose, a polyvinyl pyrrolidone, gelatin, etc. can be mentioned. In addition, this barrier layer solution can also be made to contain a mordant as mentioned above.

[0048] The obtained color-material acceptance layer can raise surface smooth nature, transparency, and paint film reinforcement after spreading desiccation by letting between roll nips pass under heating pressurization using a super calender, gloss calender, etc. However, decline in voidage needs to perform such processing by setting up few conditions in order to reduce voidage (namely, in order for ink absorptivity to fall).

[0049] Since the thickness of the color-material acceptance layer obtained as mentioned above needs to have the absorption capacity which absorbs all drops in the case of ink jet record, it is necessary to determine this in connection with the voidage of a paint film. For example, the amount of ink is 2 8 nL(s)/mm. If it is the case where voidage is 60%, film about 15 micrometers or more is needed for thickness. When this point is taken into consideration, as for a color-material acceptance layer, in ink jet record, it is desirable to have the thickness of the range of 10-50 micrometers. Since color material or a toner is adsorbed on a front face, in the case of thermal ink transfer printing or an electrophotography method, a thin film is enough, and, as for a color-material acceptance layer, it is desirable to it to have 0.1-10-micrometer thickness.

[0050] A single material is sufficient as the non-subtlety particle and water soluble resin which mainly constitute a color-material acceptance layer, respectively, and the mixed stock of two or more materials is sufficient as them. moreover, the color-material acceptance layer may contain an acid and alkali as various kinds of mineral and a PH regulator, in order are alike other than this and to raise the dispersibility of a particle, although it mainly consists of the above-mentioned inorganic particle and water soluble

resin. Moreover, various kinds of surfactants for the purpose which raises spreading fitness and surface quality may be used. In order to control surface frictional electrification and exfoliation electrification, or in order to adjust surface electric resistance in a xerography, the metallic-oxide particle with a surfactant with ion conductivity or electronic conductivity may be included. Moreover, various kinds of mat agents for the purpose which reduces a surface friction property may be included. Furthermore, various kinds of anti-oxidants for the purpose which controls degradation of color material again, the ultraviolet ray absorbent, and the singlet oxygen quencher may be included.

[0051] Moreover, an adhesive property may be raised between a color-material acceptance layer and a base material, or undercoat may be prepared on a base material for the purpose of adjusting electric resistance. In addition, a color-material acceptance layer may be prepared in both sides of a base material, in order to prepare only in one side of a base material and to control deformation of curl of the sheet for record etc. An antireflection film may be prepared in order to raise light transmission nature to the opposite side or both sides by the case where it uses by OHP etc., when preparing a color-material acceptance layer only in one side of a base material.

[0052]

[Example]

[0053] [Example 1] By the following approach, the sheet equipped with the color-material acceptance layer for ink jet record was produced.

[0054]

[Table 1]

(1) The presentation of the coating liquid for porous layer (front [ bridge formation ] color-material acceptance layer) formation (all the values of the weight section which shows the loadings of all the following coating liquid express solid content or a nonvolatile matter)

\*\* Anhydrous silica particle (primary [ an average of ] particle diameter: 7nm, 10 weight section surface silanol group:2-3 piece/nm<sup>2</sup>, refractive-index:1.45, trade name:Aerosil 300 (product made from Japanese Aerosil))

\*\* Polyvinyl alcohol (whenever [ saponification ]: 81.8%, 3.3 weight section polymerization-degree:4000, trade name-VA440 (Kuraray Co., Ltd. make))

\*\* Ion exchange water The 136.0 weight sections [0055] \*\* the polyvinyl alcohol water solution (what was dissolved in the remainder 62.7 weight section of ion exchange water) after adding in the ion exchange water (73.3 weight sections) of \*\* and distributing a silica particle for 20 minutes on condition that 10000rpm using a high-speed rotation wet colloid mill (KUREA mix (M Technique Co., Ltd. make)) -- in addition, it distributed on the still more nearly same conditions as the above, and the coating liquid for porous layer formation was obtained.

[0056] An extrusion die coater is used for the front face of the laminated paper for the photographic printing papers with a thickness of 200 micrometers for the above-mentioned coating liquid, and it is 200 cc/m<sup>2</sup>. It applied by coverage and dried for 3 minutes at 80 degrees C (3m [/second ] wind speed) with hot air drying equipment. The spreading layer showed this period and the constant rate of drying. After the desiccation for these 3 minutes, immediately, this spreading layer was made immersed in the borax content solution of following (2) for 1 second, and it dried for 10 minutes at 80 degrees

C. Thereby, desiccation thickness formed the color-material acceptance layer which is 27 micrometers.

[0057]

[Table 2]

(2) Borax content solution \*\* borax One weight section \*\* surfactant The 0.2 weight sections (trade name: F-144D, Dainippon Ink & Chemicals, Inc. make)

\*\* Diaryl dimethylammoniumchloride and diacid-izing The 1.4 weight sections Sulfur copolymerization object \*\* ion exchange water The 97.4 weight sections [0058] In the borax content solution of the [example 2] example 1, the sheet for ink jet record was similarly produced instead of diaryl dimethylammoniumchloride and a sulfur dioxide copolymerization object except having used the poly allylamine.

[0059] In the borax content solution of the [example 3] example 1, the sheet for ink jet record was similarly produced instead of diaryl dimethylammoniumchloride and a sulfur dioxide copolymerization object except having used the dimethyl-2-hydroxypropyl ammoniumchloride polymerization object.

[0060] [Example 4] The sheet for ink jet record was produced by the following approach.

[0061]

[Table 3]

Coating liquid \*\* hydroxypropyl methylcellulose for middle class formation The 5.5 weight sections (metro-ZU 90SH; viscosity great 100000 (Shin-Etsu Chemical Co., Ltd. make)) \*\* surfactant (trade name: F -144D 2.0 weight section Dainippon Ink & Chemicals, Inc. make)

\*\* Ion exchange water The 992.5 weight sections [0062] In the example 1, the coating liquid for porosity formation and a cross linking agent solution were applied three layers of coincidence by making the above-mentioned coating liquid for interlayer formation into an interlayer. The side which touches a base material using an extrusion die coater with the delivery of three slits to coating liquid 200 cc/m<sup>2</sup> for porosity formation, coating liquid 30 cc/m<sup>2</sup> for interlayer formation, and cross linking agent solution 15 cc/m<sup>2</sup> It applied three layers of coincidence by coverage, and dried for 10 minutes at 80 degrees C. Thereby, thickness formed the color-material acceptance layer which is 27 micrometers.

[0063] In the [example of comparison] example 1, except that a borax content solution did not contain diaryl dimethylammoniumchloride and a sulfur dioxide polymerization object, the sheet for ink jet record was produced similarly.

[0064] About the sheet for ink jet record obtained by [evaluation of sheet for ink jet record] above, the ink jet record fitness was evaluated by the following measuring methods.

(1) Parallel ray permeability was measured using the Hayes hazemeter (HGM-2DP; Suga Test Instruments Co., Ltd. make), and Hayes was measured. In addition, Hayes measured the color-material acceptance layer using the sheet for record formed and obtained instead of the laminated paper for the photographic printing papers used as a base material in each example and the example of a comparison on the polyethylene terephthalate film with a thickness of 100 micrometers, in order to make the measurement easy.

[0065] (2) The average was calculated by having measured using the voidage mercury porosimeter (trade name: pore sizer 9320-PC2, Shimadzu Make), and having acquired

voidage distribution.

(3) About glossiness each sheet for record, glossiness was measured according to the approach of a publication to JIS-P -8142 (75-degree specular gloss test method of paper and the paper board).

[0066] (4) With the ink rate-of-absorption ink jet printer (trade name-M-700C, Seiko Epson make), Y (yellow), M (Magenta), C (cyanogen), K (black), B (blue), G (green), and R (red) to the sheet for record carried out solid printing, the contact press of the paper was carried out just behind that (after about 10 seconds), and it judged as follows by the existence of the imprint to the paper of ink.

AA: Some ink was not imprinted by paper.

CC: Some ink was imprinted by paper.

[0067] (5) Generating each sheet for record of a cracking crack was observed visually, and it evaluated as follows according to the existence of the cracking crack generated on the front face, and its magnitude.

AA: [0068] as which the cracking crack of the die length beyond CC:3mm as which the cracking crack of the die length which is BB:1-2mm as which a cracking crack is not regarded is regarded is regarded (6) The print pattern same on the sheet for record was made to form using the same printer as measurement of waterproof ink rate of absorption, and it dipped underwater for 1 minute after 3-hour neglect, and the flow condition of ink was observed visually and evaluated as follows.

AA: -- BB: to which a color did not flow at all -- [0069] to which CC:color to which a color flows on the whole and the depth of shade is thin is flowing nearly completely The result of the above-mentioned evaluation is shown in the 1st following table.

[0070]

[Table 4]

1st Table ----- Hayes	Voidage	Glossiness	Ink	Cracking	crack																							
Water	resisting	property	(%)	(%)	(%)																							
Example 1	12.1	62	52	AA	AA	AA	Example 2	11.9	60	53	AA	AA	AA	Example 3	11.861	50	AA	AA	AA	Example 4	11.2	61	51	AA	AA	AA	Example of an AA	-----
-----	comparison	12.0	6152	AAAA	BB	-----	[0071]																					

[Effect of the Invention] The sheet for record equipped with the color-material acceptance layer of this invention can absorb liquefied ink early especially in ink jet record, and a minute image without an ink blot or ink \*\*\*\*\* not only can obtain it, but it can form simply the high-definition image which was excellent in the water resisting property in the color-material acceptance layer which is a porous layer, without causing generating of a cracking crack. Moreover, since it excels in the absorptivity of the color-material acceptance layer of the record sheet of this invention, and blot prevention, also in the various recording methods of thermal transfer recording or electrophotography record, the adhesive property of color material or a toner improves. Therefore, it can be said that the sheet for record of this invention is a sheet for record which fitted the various record approaches and was excellent in productivity.

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## TECHNICAL FIELD

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[Industrial Application] This invention relates to the sheet for record which records an image (it is a concept also containing an alphabetic character image) etc. using color

material. In order to form an image sheet by ink jet record, thermal transfer recording, electrophotography record, etc. especially, it is related with the sheet for record used advantageously.

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## PRIOR ART

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[Description of the Prior Art] In recent years, the recording method and equipment which various information processing system was developed and fitted each information system are also developed and adopted with rapid development of an information industry. It is known that lightweight-izing and the miniaturization of equipment which the thermal-ink-transfer-printing recording method using an ink jet or the ink recording method using a plotter and melting mold color material, or sublimation mold color material uses are easy, and the noise does not have them, either, and they are excellent also in operability and maintainability in such a recording method. Moreover, by such recording method, formation of a color picture is also easy. In addition, also by the record system of the conventional electrophotography method, colorization progresses, and the printer and copying machine in which full color \*\* is possible have been developed and commercialized with high resolution.

[0003] Although various kinds of methods are developed as an ink jet method, there are three sorts, the approach using the coloring matter solution (water color ink) which roughly divides and contains water-soluble coloring matter, the approach using the coloring matter solution (oily ink) containing oil solubility coloring matter, and the method of carrying out thermofusion of the low-melt point solid wax (wax ink) containing coloring matter, and using it. The mainstream is a type which uses water color ink. Any approach is the approach of forming an image by the approach of solidifying ink by making the front face of the sheet for ink record breathe out the particle drop of ink, and performing desiccation or cooling after that.

[0004] A thermal-ink-transfer-printing method is roughly divided, and has two sorts of methods. The first method by carrying out heat impression from a base material side at the shape of a pattern on the ink sheet with which the ink layer of thermofusion nature was formed on the base material It is the approach (heat-of-fusion imprint) of carrying out melting of the ink layer to the shape of a pattern, making the sheet for record imprinting the melting ink, and obtaining an image. The second method It is the approach (heat-of-sublimation imprint) of performing heat impression from a base material side into the thermal recording ingredient in which the ink layer which consists of the resin and the sublimability color of high softening temperature was formed on the base material, like the former, making a sublimation color sublimating to it in the shape of a pattern, making an ink image imprinting on the sheet for record, and obtaining an image. After giving an optical image pattern to the electrified photoconductive layer by the electrophotography method, forming an electrostatic latent image and developing negatives with a toner subsequently, the approach of imprinting a toner image on the sheet for record, and carrying out melting fixing of the toner with heat is in use.

[0005] On the other hand, it may be necessary to form an image on a transparency sheet. In this case, a transparency image is imprinted on the sheet for transparence record using either of the above-mentioned approaches using the bright film which prepared the transparent color-material acceptance (absorption) layer in the front face as a sheet for

record. By forming a transparency image on such a sheet for transparency record, the OHP film used instead of a slide, the film for a back light display used instead of a printing poster or a display board, the film for mother prints, etc. are created.

[0006] The sheet for record (bright film) in which the image (a transparency image or light transmission nature image) was formed by the above-mentioned recording method When it is required for the color material which needs to show the hue excellent in the image obtained, saturation, and lightness, and forms the image further to have pasted the front face of the sheet for record firmly and the still more minute image in the case of ink jet record is obtained Liquefied ink is absorbed early and it is required that neither an ink blot nor ink \*\*\*\*\* should be generated etc.

[0007] In order to solve these troubles, various proposals are made from the former. For example, the sheet for record which becomes JP,57-14091,A and JP,61-19389,A from the clear layer of a transparency base material, and the colloidal silica and water soluble resin which were prepared on it is proposed. However, as for this clear layer, since the particle of colloidal silica is too large and there are too many amounts of water soluble resin, voidage big enough is not obtained, but for this reason, the above-mentioned sheet for record has the problem that ink rate of absorption large enough is hard to be shown.

[0008] Moreover, the sheet for record possessing the color-material acceptance layer which has the pore formed from the quasi-boehmite particle is indicated by JP,2-276670,A and JP,3-281383,A. According to examination of this invention person, although this sheet for record showed high ink absorptivity, since the refractive index was high, it became clear that transparency high enough was not acquired.

[0009] The sheet for record which has the clear layer which becomes JP,61-53598,A from a base material, and the particle and water soluble resin of a synthetic silica and refractive indexes 1.44-1.55 which were prepared on it further again is indicated. A synthetic silica has a diameter of a primary particle usually exceeding 10nm, and an aggregated particle serves as particle size of several 100nm further. The sheet for record containing such a particle does not show light transmittance high enough that such aggregated particles tend to be scattered [ therefore ] about in light. Furthermore, since a clear layer is a big aggregated particle and it has comparatively many holes, generating of an ink blot or ink \*\*\*\*\* cannot fully be prevented.

[0010] The sheet for record with which the color-material acceptance layer which has the three-dimensional structure of the high voidage formed in JP,7-276789,A from a non-subtlety particle and water soluble resin as a sheet for record which solves the above-mentioned problem was prepared on the transparency base material is proposed. Control of the above-mentioned ink absorptivity and a color mixture blot is presupposed by this configuration that it is enough and an image with high resolution can be obtained.

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## EFFECT OF THE INVENTION

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[Effect of the Invention] The sheet for record equipped with the color-material acceptance layer of this invention can absorb liquefied ink early especially in ink jet record, and a minute image without an ink blot or ink \*\*\*\*\* not only can obtain it, but it can form simply the high-definition image which was excellent in the water resisting property in the color-material acceptance layer which is a porous layer, without causing generating of a cracking crack. Moreover, since it excels in the absorptivity of the color-

material acceptance layer of the record sheet of this invention, and blot prevention, also in the various recording methods of thermal transfer recording or electrophotography record, the adhesive property of color material or a toner improves. Therefore, it can be said that the sheet for record of this invention is a sheet for record which fitted the various record approaches and was excellent in productivity.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] This invention sets it as the main purposes to offer the non-subtlety particle and water soluble resin in which high transparency and the outstanding color-material stability are shown, or the sheet for record equipped with the becoming color-material acceptance layer.

[0012] In addition, generally, the non-subtlety particle used in the color-material acceptance layer of the high voidage formed from a non-subtlety particle and water soluble resin has a small particle, and it is [ the content of the particle in a color-material acceptance layer ] large. And when the coating liquid containing the ingredient for forming such a color-material acceptance layer was applied, while drying the spreading layer, it became clear by examination of this invention person that a cracking crack may occur. And especially this cracking crack became clear [ that it is also easy to generate when it dries at comparatively high temperature ], in order to shorten the drying time. Although the approach of making viscosity of the binder of coating liquid comparatively high is proposed by JP,9-109545,A as an approach of preventing this cracking crack, since it is easy to generate spreading nonuniformity etc. and leads to the fall of the workability of spreading formation of a color-material acceptance layer by this approach, it is not desirable. Moreover, this approach cannot be said to be enough in the cracking crack prevention effectiveness.

[0013] In order to prevent the cracking crack of the above-mentioned color-material acceptance layer, this invention person repeated examination, and the cracking crack of a spreading layer became clear [ generating at the stage shifting to decreasing drying ] in the middle of the desiccation (i.e., constant rate drying), after applying the coating liquid for color-material acceptance stratification on a base material. Based on this knowledge, this invention person repeated examination further and completed invention of the sheet for record which prepared it as early as possible as raised the film reinforcement of a spreading layer in the condition of the constant rate drying before a decreasing drying condition starts. This invention is indicated by the Japanese-Patent-Application-No. No. 296285 [ nine to ] specification. In addition, although the example which applied the silane coupling agent on porous membrane, and gave the water resisting property was shown by this application, as a result of this invention person's repeating examination, a header and this invention were reached [ that waterproof improvement is possible and ] also by applying a mordant to a cross linking agent and coincidence.

[0014] Therefore, it also sets it as the purpose that this invention can obtain an image sheet by ink jet record, thermal transfer recording, or electrophotography record, and offers the sheet for the record which has the color-material acceptance layer excellent in the water resisting property which a cracking crack cannot generate easily at the time of spreading desiccation, and can be formed simply.

[0015] Especially this invention can form a minute image, without preventing the

absorption nonuniformity of ink and generating an ink blot and ink \*\*\*\*\* by absorbing liquefied ink quickly, and it aims at offering the sheet for record equipped with the color-material acceptance layer excellent in the water resisting property which can be formed simply suitable for especially ink jet record, without a cracking crack occurring at the time of spreading desiccation.

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## MEANS

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[Means for Solving the Problem] This invention is in the sheet for record characterized by being the hardening film of the water soluble resin with which this color-material acceptance layer contains a non-subtlety particle and a mordant in the sheet for record with which the color-material acceptance layer is prepared on the base material. A color-material acceptance layer applies the coating liquid containing a non-subtlety particle and water soluble resin on a base material again, and this invention is also in the spreading and coincidence, or the above-mentioned sheet for record which is the layer obtained by giving and stiffening the solution containing the cross linking agent which can construct a bridge in water soluble resin, and a mordant before the applied layer comes to show the falling rate of drying. This invention is also in the above-mentioned sheet for record which is the layer obtained by carrying out coincidence spreading and making it harden on a base material where the barrier liquid (however, either [ at least ] the solution containing a cross linking agent or barrier liquid is made to contain a mordant) with which a color material acceptance layer consists the coating liquid containing a non-subtlety particle and water soluble resin and the solution containing a cross linking agent of a cross linking agent and an ingredient which does not react again is inserted.

[0017] The desirable mode of the sheet for record of this invention is as follows.

- (1) A cross linking agent is a boron compound (especially borax).
- (2) A non-subtlety particle is [ primary / an average of / particle diameter ] a silica particle 20nm or less (preferably 10nm or less, especially the range of 3-10nm).
- (3) Water soluble resin is polyvinyl alcohol or gelatin.
- (4) The weight ratio of a non-subtlety particle and water soluble resin is in the range of 1.5:1-10:1 (subtlety [ non- ] particle: water soluble resin).
- (5) A color-material acceptance layer has 40 - 80% of voidage (especially 50 - 80% of voidage).

[0018] (6) The sheet for record is an object for ink jet record.

(7) The coverage on the color-material acceptance layer of a cross linking agent content solution is 0.01 - 10 g/m<sup>2</sup> in the amount of cross linking agent conversions. It is in the range (especially the range of 0.05 - 5 g/m<sup>2</sup>).

- (8) A color-material acceptance layer has a three-dimensional network.
- (9) A color-material acceptance layer has 30% or less of Hayes.
- (10) The above-mentioned sheet for record for ink jet record whose thickness of a color-material acceptance layer is 10-50 micrometers.
- (11) The object for electrophotography or the sheet for the above-mentioned record for thermal recording whose thickness of a color-material acceptance layer is 0.1-10 micrometers.
- (12) The mordant contained in a color-material acceptance layer is a basic polymer.

[0019]

[Embodiment of the Invention] The sheet for record of this invention has the basic configuration which consists of a base material and a color-material acceptance layer formed on the base material, for example, can manufacture it as follows.

[0020] Opaque ingredients, such as paper, may be used, using transparent materials, such as plastics, as an ingredient which can be used as a base material. When employing the transparency of a color-material acceptance layer efficiently in this invention, as for a base material, it is desirable that they are a transparency base material or the opaque base material of high gloss. As an ingredient which can be used as a transparency base material, it is transparent and the ingredient which has the property to bear the radiant heat when being used on OHP or a back light display is desirable. As such an ingredient, cellulose ester, such as polyester; nitrocelluloses, such as polyethylene terephthalate, cellulose acetate, and cellulose acetate butylate, and polysulfone, polyphenylene oxide, polyimide, a polycarbonate, a polyamide, etc. can be mentioned. Polyester is desirable in these and especially polyethylene phthalate is desirable. About the thickness of a transparency base material, although there is especially no limit, its 50-200-micrometer thing is easy to deal with it and is desirable.

[0021] That in which the near front face in which a color-material acceptance layer is prepared has 40% or more of glossiness as an opaque base material of high gloss is desirable. The above-mentioned glossiness is JIS. It is the value calculated by measuring according to the approach of a publication to P-8142 (75-degree specular gloss test method of paper and the paper board). As an example of the opaque base material of high gloss, art paper, coat paper, cast coated paper, Paper of high gloss, such as a baryta paper used for the base material for film photos etc.; Polyester, such as polyethylene terephthalate (PET) Cellulose ester, such as a nitrocellulose, cellulose acetate, and cellulose acetate butylate Or polysulfone, polyphenylene oxide, polyimide, a polycarbonate, The film of the high gloss which plastic film, such as a polyamide, was made to contain white pigments etc., and was made opaque (surface calender processing etc. is performed), Or the film with which the enveloping layer of the polyolefine which contains white pigments or is not contained was prepared in the front face of content plastics, such as the various above-mentioned papers, the above-mentioned transparency plastic film, or white pigments, can be mentioned. Furthermore, white-pigments content foaming polyester film (calcium content foaming PET which was made to contain an example and a polyolefine particle and formed the opening by extension) can also be mentioned. Moreover, the special kind paper in which the polyolefine coat paper (paper base material with which the white-pigments content polyolefine layer was prepared in the front face) currently generally used as a base material for film photos, or a metal vacuum evaporationo layer was prepared can be used suitably. The paper base material with which the white-pigments content polyolefine layer was prepared especially, the polyester (preferably PET) film with which the white-pigments content polyolefine layer was prepared, white-pigments content polyester film, or white-pigments content foaming polyester film is desirable. Even if it attaches the thickness of an opaque base material, although there is especially no limit, a 50-200-micrometer thing is easy to deal with it and is desirable [ a limit ].

[0022] As a base material, what performed corona discharge treatment, flame treatment, and UV irradiation processing may be used.

[0023] In case the coating liquid containing a non-subtlety particle and water soluble

resin is applied on a base material, this spreading, coincidence, or before the applied this layer comes to show the falling rate of drying, as for the color-material acceptance layer of the sheet for record of this invention, it is desirable that it is the layer which the water soluble resin obtained by giving and stiffening the solution containing a cross linking agent and a mordant on a spreading layer hardened by the cross linking agent.

[0024] Moreover, the color-material acceptance layer of the sheet for record of this invention can also be obtained by carrying out coincidence spreading and making it harden on a base material, where the barrier liquid (however, either [ at least ] the solution containing a cross linking agent or barrier liquid is made to contain a mordant) which consists the coating liquid containing a non-subtlety particle and water soluble resin and the solution containing a cross linking agent of a cross linking agent and an ingredient which does not react is inserted.

[0025] The polyvinyl alcohol which is resin which has hydroxyl as a hydrophilic structural unit as an example of water soluble resin (PVA), Cellulose system resin [methyl cellulose (MC), ethyl cellulose (EC), ], such as hydroxyethyl cellulose (HEC) and a carboxymethyl cellulose (CMC), Chitins and starch; The polyethylene oxide which is resin which has ether linkage (PEO), The polyacrylamide (PAAM) and the polyvinyl pyrrolidone (PVP) which are resin which has polypropylene oxide (PPO), polyethylene-glycol (PEG), and polyvinyl ether (PVE);, an amide group, and amide association can be mentioned. Moreover, the polyacrylate which has a carboxyl group as a dissociative radical, maleic resin, alginate, and gelatin can be mentioned.

[0026] As a non-subtlety particle, a silica particle, colloidal silica, a calcium silicate, a zeolite, a kaolinite, halloysite, a muscovite, talc, a calcium carbonate, a calcium sulfate, boehmite, quasi-boehmite, etc. can be mentioned, for example. What has a refractive index in the range of 1.40-1.60 from the point of not reducing transparency is desirable. A silica particle is desirable in these. Moreover, the first [ an average of ] particle diameter of a non-subtlety particle has a common thing 20nm or less (preferably 10nm or less, especially 3-10nm), and, as for a refractive index, it is desirable that they are the 1.45 neighborhoods.

[0027] By the hydrogen bond by the surface silanol group, for an adhesion and cone reason, particles can form the structure where especially voidage is large, when especially the first [ an average of ] particle diameter is 10nm or less as mentioned above, and the ink absorption property of a silica particle improves. A silica particle is divided roughly into a wet method particle and a dry-process particle according to a manufacturing method. The method of the acidolysis of a silicate generating active silica, carrying out the polymerization of this moderately in a wet method, carrying out flocking settling, and obtaining a water silica is in use. One dry process has a method in use of obtaining an anhydrous silica by the approach (arc process) of carrying out heating hydride generation of the approach (flame hydrolysis), silica sand, and corks by elevated-temperature gaseous-phase hydrolysis of halogenation silicon with an arc in an electric furnace, and oxidizing this with air. In the case of a silicic anhydride (anhydrous silica), especially voidage is easy to form the high three-dimensional structure and is desirable [ a silica ], although the water silica and the anhydrous silica which are obtained by these approaches have a difference in the consistency of a surface silanol group, the existence of a hole, etc. and show a property different, respectively. This reason is 2 5-8 pieces/nm, when the consistency of a surface silanol group is a water silica, although it is not clear. Mostly,

when it is easy to condense a particle densely (aggregate) and it is one anhydrous silica, it is 2 2-3 pieces/nm. Since it is few, it is presumed that it is because it becomes \*\*\*\* flocculation (FUROKYU rate) and voidage becomes high structure.

[0028] When the class of resin combined with a silica particle is important and it uses an anhydrous silica from a viewpoint of transparency, PVA, especially PVA of whenever [ low saponification ] (whenever [ saponification ] is 70 - 90% preferably) are suitable from the point of light transmission nature as water soluble resin. Although PVA has a hydroxyl group in a structural unit, this hydroxyl group and the silanol group of a silica particle front face make easy to form the three-dimensional network which forms hydrogen bond and makes the aggregated particle of a silica particle a chain unit, and it is thought that the color-material acceptance layer of the structure where voidage is high is formed by this. Thus, not only the minute record which absorbs ink quickly by capillarity and has neither an ink blot nor ink \*\*\*\*\* is possible, but the obtained porous layer can paste up firmly the color material in thermal recording, and the toner in electrophotography record in ink jet record. Color material and a toner permeate in the pore of a porous layer, the geometrical anchor effect which originates in a three-dimensional network as that result generates this reason, and it is understood that it is because this fixes color material etc. firmly. Moreover, since the rate of a non-subtlety particle increases, thermal resistance is high and the embossing-proof nature in electrophotography record also has the description of being high.

[0029] The ratio (PB ratio: weight of the non-subtlety particle to the weight 1 of water soluble resin) of a non-subtlety particle (preferably silica particle) and water soluble resin has big effect also on the membrane structure of a color-material acceptance layer. If PB ratio becomes large, voidage, pore volume, and surface area (per unit weight) will become large. If PB ratio exceeds 10, there is no effectiveness over film reinforcement and the cracking crack at the time of desiccation, on the other hand, less than by 1.5, an opening should tend to be closed by resin, voidage will decrease, and ink absorptivity ability will fall. For this reason, the range of 1.5-10 is suitable for PB ratio. Like especially an OHP film, to touch the image of the sheet for record directly by hand in many cases, a color-material acceptance layer needs to show sufficient film reinforcement. In this case, as for PB ratio, it is desirable that it is especially five or less, and in order to acquire high-speed ink absorptivity with an ink jet printer, as for PB ratio, it is desirable that it is two or more, and it is suitable that it is especially in the range of 2-5.

[0030] For example, when the first [ an average of ] particle diameter carries out spreading desiccation of the coating liquid which distributed completely [ PB ratio / 2-5 ] in a water solution an anhydrous silica and water soluble resin 10nm or less, the three-dimensional network which makes the aggregated particle of a silica particle a chain unit is formed, 30nm or less and voidage can form 0.5 or more mL/g of pore specific volume, and specific surface area can form [ average pore ] easily the porous membrane of the translucency 100m<sup>2</sup> / more than g 50% or more.

[0031] The color-material acceptance layer of the sheet for record of this invention is a layer which the cross linking agent and the mordant were given to the layer (porous layer) which uses a non-subtlety particle and water soluble resin as a principal component, and water soluble resin hardened by the cross linking agent. As for grant of a cross linking agent, it is desirable to be carried out before the coating liquid layer for

porous layer formation comes to show the falling rate of drying at the same time the above-mentioned coating liquid for porous layer formation is applied. The cracking crack generated by this actuation while the spreading layer of the coating liquid for porous layer formation dries can be prevented effectively. That is, before a spreading layer comes to show the falling rate of drying at the same time the above-mentioned coating liquid for porous layer formation was applied or, the film reinforcement of a spreading layer is immediately raised sharply by a cross linking agent content solution's permeating in a spreading layer, reacting promptly with the water soluble resin in a spreading layer, and making water soluble resin macromolecule-ize (hardening). Consequently, the cracking crack generated at the time of desiccation of the spreading layer of the above-mentioned coating liquid for porous layer formation can be prevented effectively.

[0032] As an example of the cross linking agent used for formation of the color-material acceptance layer of the sheet for record of this invention borax, boric acid, and borate (an example, an orthoboric salt, InBO<sub>3</sub>, and ScBO<sub>3</sub> --) YBO<sub>3</sub>, LaBO<sub>3</sub>, Mg<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, and Co<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>, diborate (an example, Mg<sub>2</sub>B<sub>2</sub>O<sub>5</sub>, Co<sub>2</sub>B<sub>2</sub>O<sub>5</sub>) and a metaboric acid salt (an example --) LiBO<sub>2</sub>, calcium (BO<sub>2</sub>)<sub>2</sub>, and NaBO<sub>2</sub> and KBO<sub>2</sub>, tetraborate (example and Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and 10H<sub>2</sub>O) and 5 borate (an example --) KB<sub>5</sub>O<sub>8</sub>.4H<sub>2</sub>O and calcium<sub>2</sub>B<sub>6</sub>O<sub>11</sub> and 7H<sub>2</sub>O, CsB<sub>5</sub>O<sub>5</sub>, glyoxal, melamine formaldehyde (an example, a methylol melamine, alkylation methylol melamine), a methylolurea, resol resin, the poly isocyanate, etc. can be mentioned. Borax, boric acid, or borate is desirable in these. Since using it combining polyvinyl alcohol as water soluble resin causes crosslinking reaction promptly, borax, boric acid, and borate have it. [desirable]

[0033] When using gelatin as water soluble resin, the following compound known as a hardening agent of gelatin can be used as a cross linking agent. Aldehyde system compounds, such as formaldehyde, glyoxal, and a glutaraldehyde; Diacetyl, Ketone system compounds, such as cyclopentane dione; bis(2-chloro ethylurea)-2-hydroxy - 4, 6-dichloro-1,3,5-triazine, Activity halogenated compounds, such as 2 and 4-dichloro-6-S-triazine sodium salt; A divinyl sulfonic acid, A 1, 3-vinyl sulfonyl-2-propanol, N, and N'-ethylene screw (vinyl sulfonyl acetamido), Activity vinyl compounds, such as 1, 3, and 5-thoria chestnut roil-hexahydro-S-triazine; A dimethylolurea, N-methylol compound [, such as methylol dimethylhydantoin, ]; -- isocyanate system compound [, such as 1,6-hexamethylene diisocyanate, ]; -- U.S. Pat. No. 3017280 -- Aziridine system compound; indicated by 2983611 Ethyleneimino compound, such as an epoxy compound; 1, such as carboximide compound; glycerol triglycidyl ether indicated by U.S. Pat. No. 3100704, 6-hexamethylene-N, and N'-screw ethylene urea; Mucochloric acid, Halogenation carboxy aldehyde system compounds, such as a mucophenoxy KURORU acid; dioxane system compound; chromium alum, such as 2 and 3-dihydroxy dioxane, potash alum, a sulfuric-acid zirconium, chromium acetate, etc. In addition, two or more sorts can be combined and these hardening agents (cross linking agent) can also be used, even if independent.

[0034] The solution of a cross linking agent dissolves a cross linking agent in water and/or an organic solvent, and is prepared. The cross linking agent concentration in a cross linking agent solution has 0.05 - 10 desirable % of the weight, and its 0.1 - 7 % of the weight is especially desirable. Generally as a solvent of a cross linking agent, water is used. As an organic solvent, if a cross linking agent dissolves, it can be used for arbitration, for example, halocarbon system solvents, such as the ether [, such as ester; toluene, /, such as an aromatic series solvent; tetrahydrofuran, ], such as ketone; methyl

acetate, such as alcoholic; acetones, such as a methanol, ethanol, and isopropyl alcohol, and a methyl ethyl ketone, and ethyl acetate, and dichloromethane, etc. can be mentioned. [0035] In addition, in this invention, the water resisting property is raised by applying a mordant with a cross linking agent. If a mordant is added to the coating liquid for porous layer formation, condensation may be produced for the cationicity of the anion charge of the front face of non-subtlety particles, such as a silica, and a mordant, but each is prepared as an independent solution, if the approach of applying is used, there will be no worries about condensation of non-subtlety particles, such as a silica, and the selection range of a mordant will spread.

[0036] As a mordant, an amide group, an imide radical, the 1st class amino group, the 2nd class amino group, It is a compound containing at least one sort of cation radicals chosen from the 3rd class amino group, the 1st class ammonium salt radical, the 2nd class ammonium salt radical, the 3rd class ammonium salt radical, and a quarternary-ammonium-salt radical. As the example Polyvinylbenzyl trimethylammoniumchloride, polydiallyldimethylammoniumchloride, Polymethacryloyloxyethyl-beta-hydroxyethyldimethylammoniumchloride, A poly dimethylaminoethyl methacrylate hydrochloride, polyethylene RENIMIN, The poly allylamine, the poly allylamine hydrochloride, polyamide-polyamine resin, cation-ized starch, a dicyandiamide formalin condensate, a dimethyl-2-hydroxypropyl ammonium salt polymerization object, etc. can be mentioned. As for molecular weight, 1000 to about 20000 are [ these compounds ] desirable. There is an inclination for molecular weight to become insufficient [ less than 1000 / a water resisting property ], or more by 200000, viscosity becomes high and handling fitness serves as a defect.

[0037] When the coating liquid (coating liquid for porous layer formation) which uses a non-subtlety particle and water soluble resin as a principal component is applied on a base material on the occasion of manufacture of the sheet for record of this invention, it is desirable to use the approach of giving a cross linking agent so that this spreading layer may not cause a cracking crack, raising the film reinforcement of a spreading layer promptly, and giving a mordant to coincidence and raising a water resisting property. Or [ it applies the solution which contains a cross linking agent and a mordant in spreading and coincidence of the coating liquid which uses a non-subtlety particle and water soluble resin as a principal component in fact (it is desirable to make the barrier liquid which consists of a cross linking agent and an ingredient which does not react intervene between the solutions containing the coating liquid and the cross linking agent which use a non-subtlety particle and water soluble resin as a principal component in this case, and a mordant.) ] In addition, or it may make barrier liquid contain a mordant, after applying the coating liquid which uses a non-subtlety particle and water soluble resin as a principal component in this case, it is desirable to use the approach of giving the solution which contains a cross linking agent and a mordant promptly.

[0038] Next, after applying the coating liquid (coating liquid for porous layer formation) which uses a non-subtlety particle and water soluble resin as a principal component, before the spreading layer comes to show the falling rate of drying, how to give the solution which contains a cross linking agent and a mordant promptly is explained.

[0039] the coating liquid for porous layer formation -- an average of 1 [ for example, ] -- the silica particle not more than order particle diameter 10nm -- underwater -- adding (an example --) A high-speed rotation wet colloid mill (an example, KUREA mix (M

Technique Co., Ltd. make)) is used ten to 20% of the weight. For example, after carrying out distribution for 20 minutes (preferably for 10 - 30 minutes) on condition that high-speed rotation of 10000rpm (preferably 5000 - 20000rpm), A polyvinyl alcohol water solution (for example, it is set to PVA of about 1/3 weight of a silica like) can be added, and it can obtain by distributing on the still more nearly same conditions as the above. Thus, the obtained coating liquid is a homogeneity sol and can obtain the porous layer which has a three-dimensional network by forming this on a base material by the following method of application.

[0040] Spreading of the coating liquid for porous layer formation can be carried out by applying the coating liquid which added the antistatic agent etc. further by request and was obtained on a base material (film). Spreading can be performed by the well-known methods of application, such as an extrusion die coater, the Ayr doctor coater, bread coater, rod coater, knife coater, squeeze coater, a reverse roll coater, and bar coater.

[0041] After spreading of the coating liquid for porous layer formation, before the spreading layer comes to show the falling rate of drying, the solution containing the cross linking agent and mordant of this invention is applied on a spreading layer by the same approach as the above-mentioned coating liquid for porous layer formation, it can dry and the color-material acceptance layer by which this invention was hardened can be obtained. In addition, the solution containing a cross linking agent and a mordant may be given by the approach of a spray etc.

[0042] Before the above-mentioned spreading layer comes to show the falling rate of drying, the constant rate of drying which is for several minutes after immediately after spreading, and is the phenomenon in which the content of the solvent in a spreading layer decreases in proportion to time amount in the meantime is usually shown. The time amount which shows such the constant rate of drying is indicated by the chemical engineering handbook (707-712 pages, the Maruzen Co., Ltd. issue, October 25, Showa 55).

[0043] After spreading of the coating liquid for porous layer formation, the color-material acceptance layer of the sheet for record of this invention is preferably manufactured by giving the solution containing a cross linking agent and a mordant by the approach of spreading or a spray, while this spreading layer shows the constant rate of drying.

Generally desiccation after spreading of the coating liquid for porous layer formation is performed at 50-180 degrees C for 0.5 - 10 minutes (especially for 0.5 - 5 minutes).

Although this drying time naturally changes with coverage, the above-mentioned range is suitable for it.

[0044] A cross linking agent and a mordant can also be introduced into the spreading layer of the coating liquid for porosity formation that the base material which has this spreading layer is immersed in the solution which contains a cross linking agent and a mordant within the period the spreading layer indicates the constant rate of drying to be at the spreading layer of the coating liquid for porous layer formation, or by carrying out the spray coating cloth of the solution which contains a cross linking agent and a mordant in a spreading layer. Although the well-known methods of application other than the above-mentioned approach, such as a curtain flow coater, an extrusion die coater, the Ayr doctor coating machine, bread coater, rod coater, knife coater, squeeze coater, a reverse roll coater, and bar coater, can be used on the occasion of spreading of the coating liquid containing a cross linking agent and a mordant, it is desirable to use how coater does not

contact a spreading layer directly using extrusion die coater, a curtain flow coater, bar coater, etc.

[0045] The coverage on the color-material acceptance layer of the coating liquid containing a cross linking agent and a mordant is 0.01 - 10 g/m<sup>2</sup> by cross linking agent conversion. The range is common and it is 0.05 - 5 g/m<sup>2</sup>. The range is desirable. After spreading of the coating liquid containing a cross linking agent and a mordant, generally a spreading layer is heated for 0.5 - 30 minutes at 40-180 degrees C, and desiccation and hardening are performed. It is desirable to heat in 1 - 20 minutes at 40-150 degrees C. For example, when using borax and boric acid as a cross linking agent, it is desirable to perform heating at 60-100 degrees C for 5 - 20 minutes.

[0046] Next, how to apply the solution which contains a cross linking agent and a mordant in spreading and coincidence of the coating liquid (coating liquid for porous layer formation) which uses as a principal component the non-subtlety particle and water soluble resin which are the another formation approach of the color-material acceptance layer of the sheet for record of this invention is explained. This approach can be acquired when it carries out coincidence spreading on a base material as the coating liquid for porous layer formation contacts a base material, and it stiffens the solution containing the coating liquid for porous layer formation and a cross linking agent, and a mordant. Coincidence spreading of the solution containing the coating liquid for porous layer formation and a cross linking agent, and a mordant can be performed by the method of application which uses an extrusion die coater and a curtain flow coater, for example. Generally desiccation after coincidence spreading (multistory spreading) is performed by heating a spreading layer for 0.5 - 10 minutes at 40-150 degrees C, and a spreading layer is hardened. It is desirable to heat a hardening layer for 0.5 - 5 minutes at further 40-100 degrees C. For example, when using borax and boric acid as a cross linking agent, it is desirable to heat for 5 - 20 minutes at 60-100 degrees C.

[0047] When an extrusion die coater performs the above-mentioned multistory spreading, multistory is formed before two sorts of coating liquid moves to the delivery neighborhood of an extrusion die coater, i.e., a base material top. And since crosslinking reaction already tends to occur by the interface of a bilayer in case the spreading layer (multistory) of a bilayer moves to a base material, it becomes easy to generate thickening by mixing of regurgitation coating liquid near the delivery of an extrusion die coater, and trouble may be caused to spreading actuation. Therefore, in case the above-mentioned coincidence spreading is performed, it is desirable to apply it three layers of coincidence with spreading of the solution containing the coating liquid for porous layer formation and a cross linking agent, and a mordant, as the barrier layer solution (interlayer liquid) which serves as a cross linking agent from the ingredient which does not react further is made to intervene among both coating liquid. Barrier layer solution should just choose what does not react with a cross linking agent but can form liquid membrane. For example, a minute amount \*\*\*\* water solution and water can be mentioned for a cross linking agent and the water soluble resin (it is used as a thickener) which does not react. As an example of the polymer used in consideration of spreading nature, the hydroxypropyl methylcellulose, methyl cellulose, hydroxyethyl methyl cellulose, a polyvinyl pyrrolidone, gelatin, etc. can be mentioned. In addition, this barrier layer solution can also be made to contain a mordant as mentioned above.

[0048] The obtained color-material acceptance layer can raise surface smooth nature,

transparency, and paint film reinforcement after spreading desiccation by letting between roll nips pass under heating pressurization using a super calender, gloss calender, etc. However, decline in voidage needs to perform such processing by setting up few conditions in order to reduce voidage (namely, in order for ink absorptivity to fall).

[0049] Since the thickness of the color-material acceptance layer obtained as mentioned above needs to have the absorption capacity which absorbs all drops in the case of ink jet record, it is necessary to determine this in connection with the voidage of a paint film. For example, the amount of ink is 2.8 nL(s)/mm. If it is the case where voidage is 60%, film about 15 micrometers or more is needed for thickness. When this point is taken into consideration, as for a color-material acceptance layer, in ink jet record, it is desirable to have the thickness of the range of 10-50 micrometers. Since color material or a toner is adsorbed on a front face, in the case of thermal ink transfer printing or an electrophotography method, a thin film is enough, and, as for a color-material acceptance layer, it is desirable to it to have 0.1-10-micrometer thickness.

[0050] A single material is sufficient as the non-subtlety particle and water soluble resin which mainly constitute a color-material acceptance layer, respectively, and the mixed stock of two or more materials is sufficient as them. moreover, the color-material acceptance layer may contain an acid and alkali as various kinds of mineral and a PH regulator, in order are alike other than this and to raise the dispersibility of a particle, although it mainly consists of the above-mentioned inorganic particle and water soluble resin. Moreover, various kinds of surfactants for the purpose which raises spreading fitness and surface quality may be used. In order to control surface frictional electrification and exfoliation electrification, or in order to adjust surface electric resistance in a xerography, the metallic-oxide particle with a surfactant with ion conductivity or electronic conductivity may be included. Moreover, various kinds of mat agents for the purpose which reduces a surface friction property may be included. Furthermore, various kinds of anti-oxidants for the purpose which controls degradation of color material again, the ultraviolet ray absorbent, and the singlet oxygen quencher may be included.

[0051] Moreover, an adhesive property may be raised between a color-material acceptance layer and a base material, or undercoat may be prepared on a base material for the purpose of adjusting electric resistance. In addition, a color-material acceptance layer may be prepared in both sides of a base material, in order to prepare only in one side of a base material and to control deformation of curl of the sheet for record etc. An antireflection film may be prepared in order to raise light transmission nature to the opposite side or both sides by the case where it uses by OHP etc., when preparing a color-material acceptance layer only in one side of a base material.

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## EXAMPLE

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[Example]

[0053] [Example 1] By the following approach, the sheet equipped with the color-material acceptance layer for ink jet record was produced.

[0054]

[Table 1]

(1) The presentation of the coating liquid for porous layer (front [ bridge formation ]

color-material acceptance layer) formation (all the values of the weight section which shows the loadings of all the following coating liquid express solid content or a nonvolatile matter)

\*\* Anhydrous silica particle (primary [ an average of ] particle diameter: 7nm, 10 weight section surface silanol group:2-3 piece/nm<sup>2</sup>, refractive-index:1.45, trade name:Aerosil 300 (product made from Japanese Aerosil))

\*\* Polyvinyl alcohol (whenever [ saponification ]: 81.8%, 3.3 weight section polymerization-degree:4000, trade name-VA440 (Kuraray Co., Ltd. make))

\*\* Ion exchange water The 136.0 weight sections [0055] \*\* the polyvinyl alcohol water solution (what was dissolved in the remainder 62.7 weight section of ion exchange water) after adding in the ion exchange water (73.3 weight sections) of \*\* and distributing a silica particle for 20 minutes on condition that 10000rpm using a high-speed rotation wet colloid mill (KUREA mix (M Technique Co., Ltd. make)) -- in addition, it distributed on the still more nearly same conditions as the above, and the coating liquid for porous layer formation was obtained.

[0056] An extrusion die coater is used for the front face of the laminated paper for the photographic printing papers with a thickness of 200 micrometers for the above-mentioned coating liquid, and it is 200 cc/m<sup>2</sup>. It applied by coverage and dried for 3 minutes at 80 degrees C (3m [/second ] wind speed) with hot air drying equipment. The spreading layer showed this period and the constant rate of drying. After the desiccation for these 3 minutes, immediately, this spreading layer was made immersed in the borax content solution of following (2) for 1 second, and it dried for 10 minutes at 80 degrees C. Thereby, desiccation thickness formed the color-material acceptance layer which is 27 micrometers.

[0057]

[Table 2]

(2) Borax content solution \*\* borax One weight section \*\* surfactant The 0.2 weight sections (trade name: F-144D, Dainippon Ink & Chemicals, Inc. make)

\*\* Diaryl dimethylammoniumchloride and diacid-izing The 1.4 weight sections Sulfur copolymerization object \*\* ion exchange water The 97.4 weight sections [0058] In the borax content solution of the [example 2] example 1, the sheet for ink jet record was similarly produced instead of diaryl dimethylammoniumchloride and a sulfur dioxide copolymerization object except having used the poly allylamine.

[0059] In the borax content solution of the [example 3] example 1, the sheet for ink jet record was similarly produced instead of diaryl dimethylammoniumchloride and a sulfur dioxide copolymerization object except having used the dimethyl-2-hydroxypropyl ammoniumchloride polymerization object.

[0060] [Example 4] The sheet for ink jet record was produced by the following approach.

[0061]

[Table 3]

Coating liquid \*\* hydroxypropyl methylcellulose for middle class formation The 5.5 weight sections (metro-ZU 90SH; viscosity great 100000 (Shin-Etsu Chemical Co., Ltd. make)) \*\* surfactant (trade name: F -144D 2.0 weight section Dainippon Ink & Chemicals, Inc. make)

\*\* Ion exchange water The 992.5 weight sections [0062] In the example 1, the coating liquid for porosity formation and a cross linking agent solution were applied three layers

of coincidence by making the above-mentioned coating liquid for interlayer formation into an interlayer. The side which touches a base material using an extrusion die coater with the delivery of three slits to coating liquid 200 cc/m<sup>2</sup> for porosity formation, coating liquid 30 cc/m<sup>2</sup> for interlayer formation, and cross linking agent solution 15 cc/m<sup>2</sup>. It applied three layers of coincidence by coverage, and dried for 10 minutes at 80 degrees C. Thereby, thickness formed the color-material acceptance layer which is 27 micrometers.

[0063] In the [example of comparison] example 1, except that a borax content solution did not contain diaryl dimethylammoniumchloride and a sulfur dioxide polymerization object, the sheet for ink jet record was produced similarly.

[0064] About the sheet for ink jet record obtained by [evaluation of sheet for ink jet record] above, the ink jet record fitness was evaluated by the following measuring methods.

(1) Parallel ray permeability was measured using the Hayes hazemeter (HGM-2DP; Suga Test Instruments Co., Ltd. make), and Hayes was measured. In addition, Hayes measured the color-material acceptance layer using the sheet for record formed and obtained instead of the laminated paper for the photographic printing papers used as a base material in each example and the example of a comparison on the polyethylene terephthalate film with a thickness of 100 micrometers, in order to make the measurement easy.

[0065] (2) The average was calculated by having measured using the voidage mercury porosimeter (trade name: pore sizer 9320-PC2, Shimadzu Make), and having acquired voidage distribution.

(3) About glossiness each sheet for record, glossiness was measured according to the approach of a publication to JIS-P -8142 (75-degree specular gloss test method of paper and the paper board).

[0066] (4) With the ink rate-of-absorption ink jet printer (trade name-M-700C, Seiko Epson make), Y (yellow), M (Magenta), C (cyanogen), K (black), B (blue), G (green), and R (red) to the sheet for record carried out solid printing, the contact press of the paper was carried out just behind that (after about 10 seconds), and it judged as follows by the existence of the imprint to the paper of ink.

AA: Some ink was not imprinted by paper.

CC: Some ink was imprinted by paper.

[0067] (5) Generating each sheet for record of a cracking crack was observed visually, and it evaluated as follows according to the existence of the cracking crack generated on the front face, and its magnitude.

AA: [0068] as which the cracking crack of the die length beyond CC:3mm as which the cracking crack of the die length which is BB:1-2mm as which a cracking crack is not regarded is regarded is regarded (6) The print pattern same on the sheet for record was made to form using the same printer as measurement of waterproof ink rate of absorption, and it dipped underwater for 1 minute after 3-hour neglect, and the flow condition of ink was observed visually and evaluated as follows.

AA: -- BB: to which a color did not flow at all -- [0069] to which CC:color to which a color flows on the whole and the depth of shade is thin is flowing nearly completely The result of the above-mentioned evaluation is shown in the 1st following table.

[0070]

[Table 4]

1st Table	Hayes	Voidage	Glossiness	Ink	Cracking	crack
Water resisting property (%)	(%)	(%)	(%)	Rate of absorption	-----	-----
Example 1	12.1	62	52	AA	AA	AA
Example 2	11.9	60	53	AA	AA	AA
Example 3	11.8	61	51	AA	AA	AA
Example 4	11.2	61	51	AA	AA	AA
Example of an AA	-----	-----	-----	-----	-----	-----
comparison	12.0	61	52	AAAA	BB	-----